Atomic-scale understanding and design of alloys via quantum mechanics and atom probe tomography


Max-Planck-Institut für Eisenforschung GmbH
Düsseldorf, Germany
WWW.MPIE.DE
d.raabe@mpie.de

Colloquium Lecture - Institute of Metal Research, Chinese Academy of Sciences (IMR CAS)
Foundation: 1917 as Kaiser-Wilhelm-Institut

Since 1971: Basic corporate budget financed by Max-Planck-Society (50%) and Industry (VDEh) (50%)

(40% MPG, 40% VDEh, 20% third party funds)

Personnel (2010): 260

Basic science of complex alloys and processes
Scientific Board

Shareholder:
Max-Planck-Society, German Steel Institute

MPIE departments

Trustees Board

Strategy Board

MPIE

Scientific Board

Gunther Eggeler
(Fellow)

Mats Hillert
(external member)

Reiner Kirchheim
(external member)

NN
Dierk Raabe
Martin Stratmann
Jörg Neugebauer
Kai de Weldige

Administration

In-situ methods, damage, Interfaces
Microstructure Physics and Alloy Design
Interface Chemistry and Surface Engineering
Computational Materials Design

Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany
Overview

- Ab-initio based multiscale alloy design

- Examples:
  - Ultrahigh strength steels
  - Beta-Ti for implants and gum alloys
  - Fe-Si alloys for electromobility

- Self-organized nanostructuring by selective phase transformation

- Conclusions and challenges
Ab initio and crystal modeling

- **Most exact known materials theory**
- Obtain data not accessible otherwise
- Can be used at continuum scale
- Electronic rules for alloy design: add electrons rather than atoms
- Combine to atomic scale experiments
Multiscale FEM / FFT solvers

- external boundary conditions
- mesh
- elastic tensor
- phase fractions
- defect dynamics
- crystal kinematics
- orientation
- homogenization

**Equation:**
\[ \dot{\gamma} = \frac{d\gamma}{dt} = \rho_m b v \]

**Lp:**
\[ L_p = \sum_{\alpha=1}^{12} \dot{\gamma}_\alpha \hat{b}_\alpha \otimes \hat{n}_\alpha \]

**FEM:** finite Element Method; **FFT:** Fast Fourier Transform solver

Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany

Tomographic methods

Field of view

- Atom Probe Tomography
- EFTEM/EELS Tomography
- EDX Mapping Tomography
- Focused Ion Beam Sectioning (FIB/SEM plus EBSD, EDX)
- Nano SIMS

X-ray Microscopy/Tomography

Resolution

1 mm
100 µm
10 µm
1 µm
100 nm
100 nm
10 nm

Courtesy: P. Choi, MPI
Atom Probe Tomography (APT)

Laser or voltage pulse

Field evaporated ions

Tip-shaped sample (r<100 nm)

$V_{dc} = 2 \sim 15 \text{ kV}$

$m/n : \text{mass to charge ratio}$

$V_{dc} : \text{base voltage}$

$V_p : \text{pulse voltage}$

$t : \text{time of flight}$

$L : \text{distance specimen - detector}$

$\frac{m}{n} = 2e(\alpha V_{dc} + \beta V_p) \left( \frac{t}{L} \right)^2$
Field description image

Courtesy: J. Deges, MPI
Fe$_3$Al ordered phase (only Al displayed)

1/4(111) Frank dislocation loop

0.33 nm 0.25 nm

Courtesy: J. Deges, MPI
Fe$_3$Al ordered phase (only Al displayed)

Lattice plane reconstruction

Frank dislocation loop
- Ab-initio based multiscale alloy design
- Examples:
  - Ultra-high strength steels
  - Beta-Ti for implants and gum alloys
  - Fe-Si alloys for electromobility
- Self-organized nanostructuring by selective phase transformation
- Conclusions and challenges
From atomistic understanding towards designing new materials

D. Raabe et al. Scripta Materialia 60 (2009) 1141
Ab-initio methods for the design of high strength steels

Stress $\sigma$ [MPa] vs. Strain $\varepsilon$ [%]

- **martensite formation**
- **TRIP steel**
- **twin formation**

**TRIP steel** and **TWIP steel**

Courtesy: T. Hickel, MPI
\[ \tau_{tw} = \frac{\gamma_{sfe}}{3b_s} + \frac{3Gb_s}{L_0} \]
Stress shielding

Elastic Mismatch:
Bone degeneration, abrasion, infection
Design-task: reduce elastic stiffness

Bio-compatible elements

From hex to BCC structure: Ti-Nb, ...

Construct binary alloys in the hexagonal phase

Ti hcp phase

15/1 Ti:X ratio

14/2 Ti:X ratio

Ti atoms

substituent X

Construct binary alloys in the cubic phase

Ti bcc phase

15/1 Ti:X ratio

14/2 Ti:X ratio

Ti atoms

substituent X
MECHANICAL INSTABILITY

Ultra-sonic measurement exp. polycrystals bcc+hcp phases

Ti-hex: 117 GPa

theory: bcc polycrystals

XRD
DFT

Elastic properties / Hershey homogenization

Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany

Ab initio alloy design: Elastic properties: Ti-Nb system

Young’s modulus surface plots

$A_z = 2 \frac{C_{44}}{C_{11} - C_{12}}$

**Ti-18.75at.%Nb**

- $A_z = 3.210$
- Ti: 115 GPa
- Ti – 35 Nb - 7 Zr - 5 Ta: 59.9 GPa (elastic isotropic)

**Ti-25at.%Nb**

- $A_z = 2.418$

**5at.%Nb**

- $A_z = 1.058$

**Pure Nb**

- $A_z = 0.5027$

Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany

More than one million hip implants per year:

elastically compliant Titanium-alloys can reduce surgery
Nano-precipitates in soft magnetic steels

Nano-precipitates (Cu) in Fe-Si steel with Cu nano-precipitates

- Size of Cu precipitates (nm): 15 nm
- Magnetic loss (W/kg)

Nanoparticles too small for Bloch-wall interaction but effective as dislocation obstacles

Mechanically very strong soft magnets for motors
Steels for electromobility: precipitates vs. Bloch walls

Cu 2 wt.%

450°C aging

Iso-concentration surfaces at Cu 11 at.%
There are about 40 million cars in Germany

High strength soft magnetic steels in car engines and transformers reduce CO$_2$ emission
- Ab-initio based multiscale alloy design

- Examples:
  - Ultrahigh strength steels
  - Beta-Ti for implants and gum alloys
  - Fe-Si alloys for electromobility

- Self-organized nanostructuring by selective phase transformation

- Conclusions and challenges
Self-organized nanostructuring by selective phase transformation

Driving force for solute decoration of interfaces

- Gibbs adsorption isotherm: equilibrium segregation (grain boundary)
- Local partitioning in equilibrium plus kinetic freezing (interfaces)

Local phase transformation
Effect of aging on ductility

Engineering Stress (MPa)
Engineering Strain (%)

aged 450°C/48h

as-quenched

1. strain 0%
2. strain 15%

Precipitation hardening

increase of austenite fraction during aging

Engineering Strain (%)

α-Fe (Martensite)
γ-Fe (Austenite), vol. fraction 15-20%

<table>
<thead>
<tr>
<th>C</th>
<th>Ni</th>
<th>Mo</th>
<th>Ti</th>
<th>Al</th>
<th>Mn</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>2.0</td>
<td>1.0</td>
<td>1.0</td>
<td>0.15</td>
<td>12</td>
<td>bal.</td>
</tr>
</tbody>
</table>

Max-Planck-Institut für Eisenforschung, Düsseldorf, Germany
D. Raabe et al. Scripta Materialia 60 (2009) 1141
Effect of cold rolling after aging

Why so much austenite 120 K below equilibrium transformation?

\( \gamma \rightarrow \alpha' \) (TRIP)

\( \gamma \) formation during aging (450°C/48h)

12MnPH X-Ray

Fraction of Austenite (%)

Cold Rolling Reduction, %

D. Raabe et al. Scripta Materialia 60 (2009) 1141
APT results: Atomic map (12% Mn, aged 450°C/48h)

Mn atoms
Ni atoms
Mn iso-concentration: 18 at.%

70 million ions
Laser mode (0.4nJ, 54K)
Thermo-Calc \Rightarrow 

equilibrium Mn-conc.: 

- 27 at. % Mn in austenite (A)
- 3 at. % Mn in ferrite (martensite) (M)

nominal 12 at. % Mn depletion zone

Mn iso-concentration (18 at. % Mn)
precipitates in $\alpha'$

\[ x_{\text{Diff}} \approx 2\sqrt{D_t} \approx 30 \text{nm} \]

no precipitates in austenite

\[ x_{\text{Diff}} \approx 2 \text{nm} \]
Thermo-Calc ⇒
equilibrium Mn-conc.:
27 at. % Mn in austenite (A)
3 at. % Mn in ferrite (martensite) (M)

Excellent agreement between experiment & simulation!
Ultra high strength and corrosion resistance

650 MPa to 2 GPa

Fe-13.6Cr-0.44C (wt.%)
at 5.45 at.% C, austenite forms at 400°C

C has ‘\(\backslash\)’ shape in austenite layer: inheritance from austenite, Gibbs adsorption isotherm;  
C on martensite grain boundaries

C has ‘\(\vee\)’ shape in austenite layer: austenite reversion through partitioning and kinetic freezing
Microstructure development

400°C
1 min

1 μm
Microstructure development

Prior Austenite Grain Boundary

400°C 1min
Self-repair steels
70% of all industrial innovations are associated with progress in materials science and engineering

Metallic materials occupy key roles in:
energy, transportation, health, safety, infrastructure

Our mission: Designing new alloys from first principles
- Multiscale simulation
- Multiscale characterization starting from the atomic scale
- Synthesis, processing, testing